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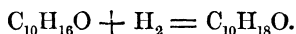
CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

ON THE REDUCTION OF CAMPHOR TO BORNEOL.

BY C. LORING JACKSON.

Communicated November 12th, 1884.

IN 1883, Menke and I published a paper * entitled "A New Method of Preparing Borneol from Camphor," in which we described, first, the complete reduction of camphor to borneol by sodium and moist toluol; secondly, a convenient practical method for making borneol by the action of one and a third times the theoretical amount of sodium on an alcoholic solution of camphor, and purifying the product by crystallization from hot alcohol; and thirdly, explained the formation of the borneol by the following reaction:—



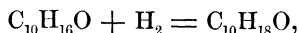
In the first number of the Monatshefte für Chemie † for this year, Kachler and Spitzer published an examination of our method, which led them to the conclusion that it was worthless, since in three experiments they obtained products, the larger part of which melted from 179° to 181°, and in no case higher than 185° even after fractional crystallization and sublimation (borneol melts at 199½°); while another set of experiments showed that as much as 82.8% of the hydrogen evolved by the sodium in one case, and 54.1% in another, escaped in the free state. They also determined how much borneol had been formed in one of their experiments, by converting the crude product into chlorides, and determining the chlorine, which showed 22.8% of borneol to 77.2% of unaltered camphor; and therefore doubt whether the formation of borneol was due to reduction by nascent

* These Proceedings, Vol. XVIII. p. 93.

† Monatshefte für Chemie, No. 5, p. 50.

hydrogen at all, but ascribe it rather to the action of the sodium itself, as if in the presence of an indifferent liquid (Baubigny's reaction).

It is to be remarked, however, that they have confined their attention to the reduction of camphor by sodium and alcohol, and were not justified in thus rejecting our reaction,



as they had not repeated the experiment described in the beginning of our paper, in which 25 g. of camphor by the action of an excess of sodium and moist toluol were completely converted into borneol, as shown by the melting-point 197–198°, and a combustion. That this observation, and therefore the reaction given above, are correct, has been proved by Immendorff under the direction of Anschütz, who has published a most welcome paper* on the subject in the interval between the appearance of Kachler and Spitzer's paper and this answer, which has been much delayed, because, since the publication of their paper, I have had no laboratory at my disposal until this autumn. Immendorff's proof consisted in increasing the amount of sodium used upon the alcoholic solution of camphor from $1\frac{1}{3}$ to $3\frac{1}{3}$ times the theoretical amount, when he obtained a product, which, after crystallization from petroleum ether or sublimation, melted at 199–200°, and was proved to be pure borneol by analyses of its chloride. Although in this way he confirms our theoretical views, he did not obtain better results from our practical process than Kachler and Spitzer, as he got as low a melting-point (181°) as they, when he used the amount of sodium recommended by us ($1\frac{1}{3}$ times the theory), and even with twice the theoretical amount did not get a melting-point above 188°. As we had got a melting-point of 193° for the crude product, I felt that it was advisable to take up the subject again, and study the conditions of the reaction more carefully, especially as both Kachler and Spitzer and Immendorff dwell on the interest of this process from a theoretical as well as a practical point of view.

The result of my experiments is, however, that, even when in following our original directions I tried to make the conditions as unfavorable as possible, the melting-point of the crude product was 187–188°, and in other repetitions 188° and 189°, so that my products with one and a third times the theory of sodium melted 6° to 8° higher than the corresponding ones of Immendorff, and as high as his with twice the theory,† but not so high as our previous melting-point of 193°. Although,

* Ber. d. ch. G., xvii. p. 1036.

† With twice the theory I obtained melting-point 194°.

as I could not get such low melting-points as the foreign chemists, I have been unable to find the cause of the difference between their results and ours, I have succeeded in modifying the process for making borneol, so as to make it superior even to the much improved form given to it by Immendorff; for I soon found that a better result was obtained if less alcohol was used, and upon reducing the quantity by one half, that is, using five times the weight of the camphor, instead of ten times, as we advised originally, I obtained with one and a third times the theory of sodium a product * melting at 193° without purification, while increasing the sodium to twice the theory gave me the same result as Immendorff's with the larger quantity of alcohol, and three and a third times the theory, that is, a crude product having the melting-point 196° , which was not raised by the use of more sodium, and gave by one crystallization from ligroine † 52%, and in a second case 45%, of pure borneol, melting between 199° and 200° . This same melting-point was obtained in four different experiments; and that the yield was not better from Immendorff's method was proved by following his directions carefully in another experiment, the product of which gave, after treatment with ligroine, not more than 50% of pure borneol. I should judge, too, from the results of my experiments, that cooling and stirring the liquid had a favorable action on the process, but their effect is comparatively small.

The work described above has led me to the following method for the preparation of borneol from camphor, which becomes in this way one of the simplest and easiest operations in organic chemistry:— 10 g. of camphor are dissolved in 50 g. of common alcohol in a small beaker, and treated with 6 g. of sodium added in pieces of from 0.1 to 0.2 g. At first, only two pieces are added at a time, the addition of fresh sodium taking place only after what has been already put in has disappeared; but after the fourth gramme, a gramme may be added at once, cut in pieces of the size mentioned above. The object should be to keep up a gentle effervescence, and it is well to stir the liquid frequently, to keep it cool by immersing the beaker in a dish of water, and toward the end of the process, when the action has become sluggish, to add from time to time a few drops of water to prevent the liquid from becoming pasty. After all the sodium has been

* As this substance is identical with the crude product described in my paper with Menke, I am inclined to think that we must have used less alcohol than the amount recommended by us in that paper.

† The crystallization from ligroine, as recommended by Immendorff, is far superior to the crystallization from hot alcohol, used by Menke and me.

used up, the crude borneol is precipitated by water, washed till free from alkali, dried by pressure between cloth or filter-paper, and purified by crystallization from ligroine.

Finally, I would add that sodium amalgam reduces an alcoholic solution of camphor, although the action is so slow that it is of no value as a practical method, the melting-point being raised only to 183° by action during two weeks, part of the time on the water-bath. The fact however deserves mention, because in Beilstein's Handbuch, p. 1763, it is stated that sodium amalgam does not act on camphor.